ELECTROGENERATIVE PROCESS FOR THE RECOVERY OF GOLD FROM CYANIDE SOLUTIONS AND THE FORMATION OF GOLD MICROSTRUCTURES ON CARBON-BASED MATRICES

By

YAP CHIN YEAN

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a	proportional constant
A	nuclei rate constant, s^{-1}
A	effective electrode surface area, m^2
A_s	active electrode area per unit reactor volume, m^{-1}
A_e	specific surface area of cathode, m^{-1}
A_x	cross sectional area, cm^2
b	Reynolds exponent
c	metal concentration, mol cm^{-3}
c_O	concentration of species being oxidize
c_R	concentration of species being reduce
c_0	initial metal ion concentration, mol cm^{-3}
c_t	metal ion concentration at time t, mol cm^{-3}
C	calibration constant of viscometer, $mm^2\ s^{-2}$
D	diffusion coefficient, $cm^2\ s^{-1}$
E^o	standard reduction potential, V
E^o_{cell}	overall cell potential, V
E_a	standard reduction potential at anode, V
E_c	standard reduction potential at cathode, V
E_{co}	cross-over potential, V
F	Faraday‘s constant, 96485.309 C mol^{-1}
ΔG^o	standard Gibb‘s free energy, kJ mol^{-1}
h	height of the monolayer of deposit, cm
i	current, A
i_m	maximum current, A
i_p	peak current, A
j	current density, A cm^{-2}
j_c	cathodic current density, A cm^{-2}
j_m	maximum current density, A cm^{-2}
j_o	exchange current density at equilibrium potential, A cm^{-2}
$k‘_g$	vertical growth rate constant, mol $cm^{-2}\ s^{-1}$
k_g	lateral growth rate constant, mol $cm^{-2}\ s^{-1}$
k_m	mass transport coefficient, m s^{-1}

K	formulation constant for metal complexes
M	atomic weight, g mol^{-1}
n	the number electron accepted or release by reaction per mole of reactant
N	number of nuclei, cm^{-2}
N_0	saturation nucleus density, cm^{-2}
Q	volumetric flow, cm^3 s^{-1}
Q_{nucl}	charge density due to the 2D nucleation process, C cm^{-2}
R	correlation coefficient
R	universal gas constant, 8.31451 J K^{-1} mol^{-1}
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	time, s
t_m	time associated with maximum current, s
T	absolute temperature, K
V_e	cathode volume, m^3
V_R	volume of electrolyte, m^3
Φ_m	local potential in the solid phase, V
Φ_s	local potential in the liquid phase, V
α	charge transfer coefficient
ε	porosity of electrode
η	overpotential, V
ρ	density of metal deposit, g cm^{-3}
μ	dynamic viscosity, kg $m^{-1}s^{-1}$
ν	kinematic viscosity, mm^2 s^{-1}
v	scan rate of the potential, V s^{-1}
υ	linear flow velocity, m s^{-1}

PROSES ELEKTROGENERATIF UNTUK PEROLEHAN SEMULA EMAS DARIPADA LARUTAN SIANIDA DAN PEMBENTUKAN EMAS MIKROSTRUKTUR PADA MATRIKS BERASASKAN KARBON

ABSTRAK

Sistem elektrogeneratif telah diperkenalkan sebagai kaedah alternatif untuk perolehan semula emas daripada larutan akueus secara elektrokimia. Proses ini tidak memerlukan bekalan tenaga luar kerana pertukaran kimia berlaku secara spontan, malah pada masa yang sama, tenaga elektrik telah dihasilkan sebagai suatu produk sampingan. Dua jenis mod operasi telah dikaji. Reaktor statik yang beroperasi dalam mod elektrogeneratif telah digunakan untuk perolehan semula emas daripada larutan sianida. Larutan emas sianida digunakan sebagai katolit dalam kajian ini kerana larutan sianida merupakan agen pengekstrakan yang paling biasa digunakan dalam industri hidrometalurgi. Reaktor statik yang dilengkapkan dengan katod tiga dimensi iaitu grafit berliang dan karbon kekaca berongga (RVC) dan katod dua dimensi iaitu kuprum dan keluli telah digandingkan dengan anod zink. Sistem ini berupaya memperolehi lebih daripada 90% emas dalam masa 3 jam beroperasi. RVC yang diaktifkan merupakan katod yang paling efektif dengan kadar perolehan emas sebanyak 99% dalam satu jam beroperasi. Reaktor elektrogeneratif alir laluan yang dilengkapi dengan RVC yang diaktifkan telah dikaji. Reaktor tersebut mempunyai kadar perolehan emas lebih daripada 99% dalam masa 4 jam beroperasi. Penilaian prestasi reaktor ini adalah berdasarkan kepekatan $KAu(CN)_2$ awal dalam larutan sianida iaitu 0.051 mM, 0.508 mM , 2.54 mM dan kadar alir katolit. Berasaskan keadaan eksperimen, kadar perolehan semula emas sangat bergantung kepada kepekatan awal emas dan kadar alir katolit.

Kinetik untuk proses elektropengenapan merupakan gabungan beberapa jenis proses penukleusan yang melibatkan penjerapan, proses penukleusan dua atau tiga dimensi yang dikawal oleh pembauran atau kemasukan kekisi oleh ad-atom. RVC yang diaktifkan dengan larutan Sn/Pd mempunyai saiz partikel yang lebih kecil. Pengaktifan ini menggalakkan proses penukleusan dua dimensi dan nukleus emas akan membentuk di atas tapak aktif Sn/Pd dan tumbuh secara lateral. Pembentukan elektrogeneratif emas menghasilkan saiz emas dalam julat 20-200 nm. Ia boleh digunakan sebagai cara alternatif untuk menghasilkan mangkin emas di atas substrat berongga tiga dimensi.

ELECTROGENERATIVE PROCESS FOR THE RECOVERY OF GOLD FROM CYANIDE SOLUTIONS AND THE FORMATION OF GOLD MICROSTRUCTURES ON CARBON-BASED MATRICES

ABSTRACT

The application of an electrogenerative system as an alternative to the electrochemical recovery of gold from aqueous solutions is presented. This process does not require an external supply of energy due to the spontaneous chemical reaction that takes place in the reactor while generating an external flow of current as a by-product. Two types of operation modes were investigated. A batch reactor operating in an electrogenerative mode is used in gold recovery from cyanide solutions. In this study, gold cyanide solutions serve as the catholyte because cyanide is the most common leachant used during the extraction of metals in the hydrometallurgical industry. The batch reactor with an improved design using three dimensional cathodes namely porous graphite and reticulated vitreous carbon (RVC) and two dimensional cathode materials, copper and stainless steel plates were coupled with a zinc anode. The system resulted in more than 90% gold being recovered within 3 h of operation. Activated RVC serves as a superior cathode material having the highest recovery rate with more than 99% of gold being recovered in 1 h of operation. An electrogenerative flow-through reactor with an activated RVC cathode was also developed. The reactor proved to be efficient in recovering more than 99% of gold within 4 h of operation. The performance of the reactor was evaluated with initial $KAu(CN)_2$ concentrations of 0.051 mM, 0.508 mM , 2.54 mM and various electrolyte flow rates. Gold recovery was found to be strongly dependent on electrolyte flow rate and initial gold concentration in the cyanide solution under the experimental conditions used.

The kinetics of the gold electrodeposition process can be described by a combination of different kinds of parallel nucleation processes namely adsorption, two dimensional or three dimensional nucleation process controlled by diffusion or lattice incorporation of ad-atoms. It was found that activation of RVC using Sn/Pd activation significantly decreased the particle sizes and promotes the 2D nucleation process where the gold nuclei will be preferably formed at the Sn/Pd active sites and grow laterally. Electrogenerative gold deposition produced gold deposits with size ranging from 20-200 nm. It could serve as a potential alternative method for gold catalyst formation on 3D microporous substrates.

CHAPTER 1 INTRODUCTION

1.1 Metal Ions Removal and Recovery from Process Solutions.

Metal finishing, electronics and hydrometallurgical industries are major sources of metal ion containing process streams. The report by United States-Asia Environmental Partnership (2002) stated that chemical and electronic industries in Malaysia account for 12% of the country‘s major industrial polluters. According to the report, the local small to medium electronics and electroplating industries were found to dispose effluents containing heavy metal contaminants into domestic sewage drains without prior treatment. A cost effective treatment system is needed to recover and remove heavy metal ions from the industrial process streams. There is a trend in the metal finishing and processing industries to operate in a close-loop system (Pletcher and Walsh, 1993). The system is designed with complete recycling of excess reagents to ensure maximum utilization and minimal waste generation.

There are several methods available for metal ions removal and recovery from process solutions. Among these techniques, precipitation is the most widely due to its simplicity and cost effectiveness. The solution pH is adjusted to the optimum range for precipitating the metal as a hydroxide. Other reagents such as sulphides are added to increase recovery. Metals such as copper and chromium have been removed from wastewater using precipitation methods. Hexavalent chromium has to be reduced to trivalent chromium by sodium bisulphite or sulphur dioxide (Cherry, 1982). The subsequent process involved adding lime and caustic soda to increase the pH and precipitating the chromium as chromium hydroxide. The process is not selective, hence giving rise to a mixture of different metal precipitates. Treated water

is run through a clarifier to settle the solids. This method generates secondary pollution and involves high cost of sludge disposal in landfills.

Electrodialysis is a process involving an array of ion exchange membranes positioned between a pair of electrodes. The applied voltage drives the flow of ions in solution and the membrane selectively transports ions having positive or negative charges and reject ions of the opposite charge. Removal, separation and pre-concentration of ions can be achieved using this method. The electrodialysis method was applied in removal and recovery of nickel and copper ions from wastewater. (Ogutveran *et al.*, 1997; Spoor *et al.*, 2002; Wong *et al.*, 2002; Cifuentes *et al*, 2004). Millmam and Heller (1982) demonstrated the successful application of the electrodialysis method in a gold plating operation. Electrodialysis was operated at the drag-out rinse following the plating bath. Ion exchange resins were used for the second rinse to recover the remaining gold. Gold recoveries up to 99% were achieved and the concentrate recovered by electrodialysis was returned directly to the plating tank. However, there is a problem about membrane durability which can potentially increase cost.

Anion exchange resins have been used for the recovery of gold from cyanide solutions. The solution pH is adjusted and the solution flows through an immobile resin. Ions of interest from the solution are exchanged for similarly charged ions attached to the resin. Although such resins have higher loading capacities than activated carbon, they are much more expensive and their use involves special resin regeneration and elution processes (Gomes *et al.*, 2001). This process has failed to gain wide acceptance compared to adsorption on activated carbon due to its higher

capital cost, poor physical strength of resin and less selectivity. Exhausted resin will need to be incinerated and this process will generate environmentally hazardous fumes.

Adsorption is another method which is widely employed in metal recovery. Gold cyanide or gold chloride complexes are strongly adsorbed on activated carbon (Cho *et al.*, 1979; Adam and Fleming, 1989; Jia *et al.*, 1998). Although the mechanism has not been fully explained, this recovery system has gained wide acceptance in the gold mining industry. Heap leaching of gold with alkaline sodium cyanide in mining industries will typically produce very dilute solutions containing 0.5-10 mg L^{-1} of gold(I). The pregnant solution is then transferred to a series of tanks, where carbon is added. The gold is adsorbed onto the surface of the carbon. The carbon, with gold attached, is removed by screening. The gold bearing carbon is then passed through a stripping vessel containing heated sodium hydroxide-cyanide-water solution where the gold is desorbed. After the stripping process, the activated carbon can be regenerated. This preconcentration step will subsequently produce solutions of 50-2500 mg L^{-1} of gold(I). Gold ions eluted from the adsorbents are not in their metallic state and will be subjected to electrolytic recovery or cementation (Stavart *et al.*, 1999; Barbosa *et al.*, 2001).

Cementation has been used in metal recovery in hydrometallurgical processes. It is a metal displacement reaction where metal ions from an aqueous solution are precipitated spontaneously by a relatively more electropositive metal. Zinc dust was used in the Merrill-Crowe process to recover gold from cyanide solution. The overall chemical reaction for this process is shown in Eq. 1.1.

$$Zn + Au(CN)_2^- + H_2O + 2CN^- \rightleftharpoons Au + Zn(CN)_4^{2-} + OH^- + 0.5\ H_2 \qquad (1.1)$$

The solution is deoxygenated and soluble lead salts are added to the solution to inhibit passivation of the zinc surfaces which increase the cementation rate (Yannopoulos, 1991). Unfortunately, the resulting product is physically inseparable.

In moving towards technologies that are both efficient and environmental friendly, electrochemical methods offer the most promising options. Metal ions can be removed and recovered in a single step. Electrochemical technology plays many important roles in environmental protection and covers a broad range of technologies which are summarized in Table 1.1 (Pletcher, 1992; Pletcher and Walsh, 1993). Electrolytic methods are mostly employed in industries such as in metal refining and recycling or water treatment. However, electrolytic processes have limitations when dealing with low metal ion concentrations. In wastewater treatment and hydrometallurgical processes, the concentration of metal bearing solutions ranges from 1 mg L^{-1} to 1000 mg L^{-1}. In dilute solutions, the current efficiency of the system is very low due to the side reactions occurring in the system. The power consumption in treating dilute solutions is relatively high and thus it is not cost effective (Pletcher, 1992).

There are numerous research papers dealing with the electrowinning of gold, either from mining industries or electroplating wastes (Stavart *et al.*, 1999; Barbosa *et al.*, 2001; Reyes-Cruz *et al.*, 2002, 2004; Spitzer and Bertazzoli, 2004). Stavart *et al.* (1999) used three-dimensional carbon felt for electrowinning gold where

Table 1.1 Scope of electrochemical techniques.

Scope and details
Metal Extraction, refinery, and production • Extraction of precious metals from sulphide ores, electrorefining of copper, lead, silver, nickel, electrowinning, cementation, aluminum recycling.
Water treatment • Effluent treatment: Removal of toxic metals or organic chemicals from industrial waste streams using electrodialysis or electrolysis techniques prior to discharge. • Water disinfection: Ozonation, chlorination, hydrogen peroxide for removal of bacteria. • Recycling of process stream: Aim to regenerate redox reagents in the industrial process to achieve ‚zero effluent'.
Metal finishing and materials processing • Electroplating and electroless deposition, conversion coating forming suitable passive films such as in anodizing and chromating. Electroforming, electrochemical etching and cleaning.
Selective Chemical synthesis • Chlor/alkali manufacturing processes, organic electrosyntheses such as hydrodimerization of acrylonitrile, reduction of carboxylic acid.
On site generations of chemicals • Chlorine and hydrogen peroxide can be generated on site avoiding hazards of transporting chemicals.
Cleaner energy generation • Fuel cells, solar photovoltaic cells.
Sensors • Electrochemical sensors are available for a wide range of gases in atmosphere such as CO, SO_2, NH_3, NO_x

Sources: Pletcher, 1992; Pletcher and Walsh, 1993

gold extraction higher than 90% and current efficiencies ranging from 6% to 12% were achieved. Spitzer and Bertazzoli (2004) used a filter-press type electrochemical reactor to recover silver and gold selectively from electroplating effluents. Current efficiencies were found to be 15%-23%. Reyes-Cruz *et al.* (2004) studied gold and silver recovery from a three-dimensional electrochemical reactor with RVC electrodes and recovered 26% gold and 48% silver. All these treatment technologies are categorized as electrolytic cells, which need power consumption. Electrolytic systems involving low concentrations of gold will have kinetics and thermodynamics limitations even though the conductivity of the solution is high. Side reactions such as oxygen and water reduction tend to occur which cause low current efficiencies in all these systems (Reyes-Cruz *et al.*, 2004; Spitzer and Bertazzoli, 2004). An alternative for electrochemical methods that can reduce operating cost for the precious metal recovery process would be the electrogenerative system. This method enables recovery of metals without any external supply of energy.

1.2 Electrogenerative System and its Working Principle

An electrogenerative reactor is a galvanic reactor. The galvanic process is an electrochemical process in which a chemical reaction that occurs in a system produces an electrical current. The equilibrium potential is obtained by subtracting the potential of cathode to anode and is related to the free energy of the overall cell reaction by following Eq. 1.2

$$\Delta G^{o} = -nF E^{o}_{cell} = -nF\,(E_c - E_a) \qquad (1.2)$$

where ΔG^{o} is the Gibb's free energy, n is the number electrons accepted or released by the reaction per mole of reactant, F is Faraday's constant, E^{o}_{cell} is the overall cell potential, E_c is the standard reduction potential at cathode, E_a is the standard reduction potential at anode.

All electrogenerative processes have a negative Gibb's free energy ($\Delta G < 0$) which means that they are thermodynamically favorable and are spontaneous redox reactions. As with all electrochemical techniques, the electrogenerative reactor is an elegant technology as the main reagent being the electron is a clean reagent.

1.3 Electrogenerative Reactors

Electrogenerative reactors incorporate two coupled electrode reactions. The electrical circuit is shown in Figure 1.1. The electrical contact is made through an external wire and current collectors attached to the anode and cathode. A voltmeter is used to measure the overall cell voltage. Generally, by the careful choice of anode and cathode materials, any redox reaction which is thermodynamically favourable can be utilized for metal recovery. Selectivity and the rate of the reaction can be controlled by varying the electrode potential using a resistance load in the circuit, using suitable electrodes and electrocatalysts. In electrolytic cells, the selectivity of the system depends on the cathode potential applied to the electrode. Electrogenerative processes can be made selective for particular reactions from the choice of electrodes and electrolytes used by the system.

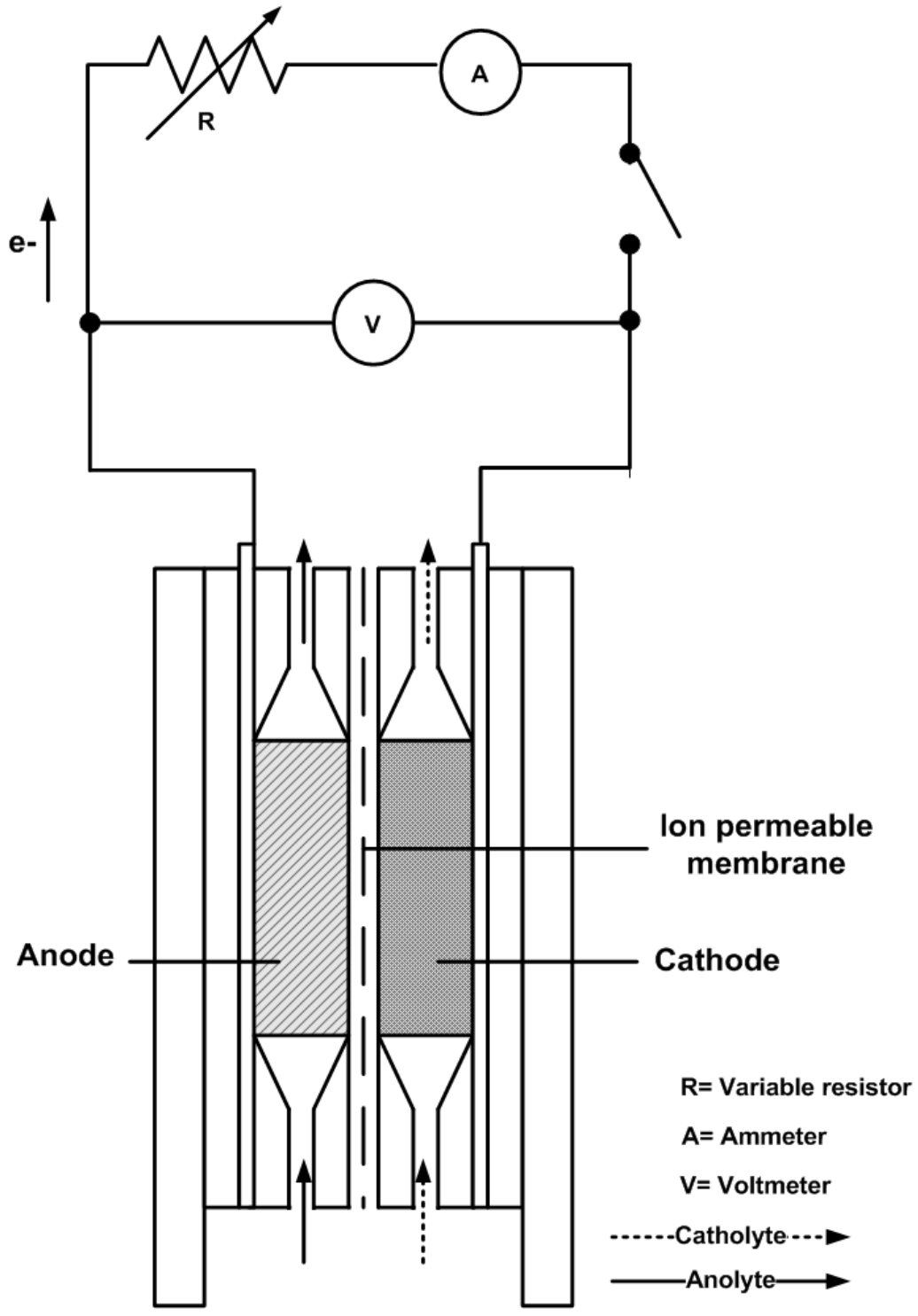

Figure 1.1 Schematic diagram of an electrogenerative reactor and its electrical circuit.

1.3.1 Reactor Design and Operation Modes

Operation of electrogenerative reactors involves many of the concepts of fuel cells and the factors considered in electrolytic cell design can also be applied to electrogenerative reactors. Electrogenerative reactors can be operated in a batch or continuous mode such as a batch reactor, single-pass reactor and batch-recycle reactor.

1.3.1.1 Flow-through and Flow-by Reactor

The flow reactor can be classified in two groups: flow-through or flow-by systems (Pletcher and Walsh, 1992). The classification is based on the direction of solution flow with respect to the electrical current through the anode and cathode. When the direction of the solution flow and electrical current flow is perpendicular to each other, it is called a flow-by system. If these directions are parallel to each other, it is called a flow-through system. Figure 1.2 shows the schematic diagram of a flow-through and a flow-by system with respect to the directions of current and solution flow. The reactors shown in Figure 1.2 contain two compartments in the cell assembly. The reactor can be assembled with multiple electrode pairs or multiple reactors which can be connected in series or in parallel to increase cell performance. The configurations of the reactor in which the electrode pairs are in parallel and in series are shown in Figure 1.3 and Figure 1.4 respectively.

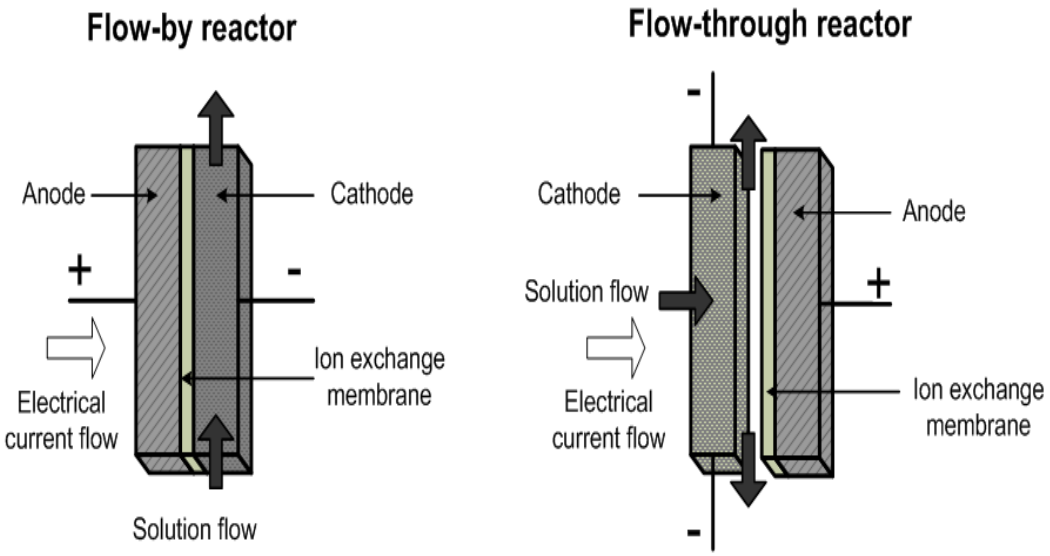

Figure 1.2 Flow-by and flow-through reactor configurations.

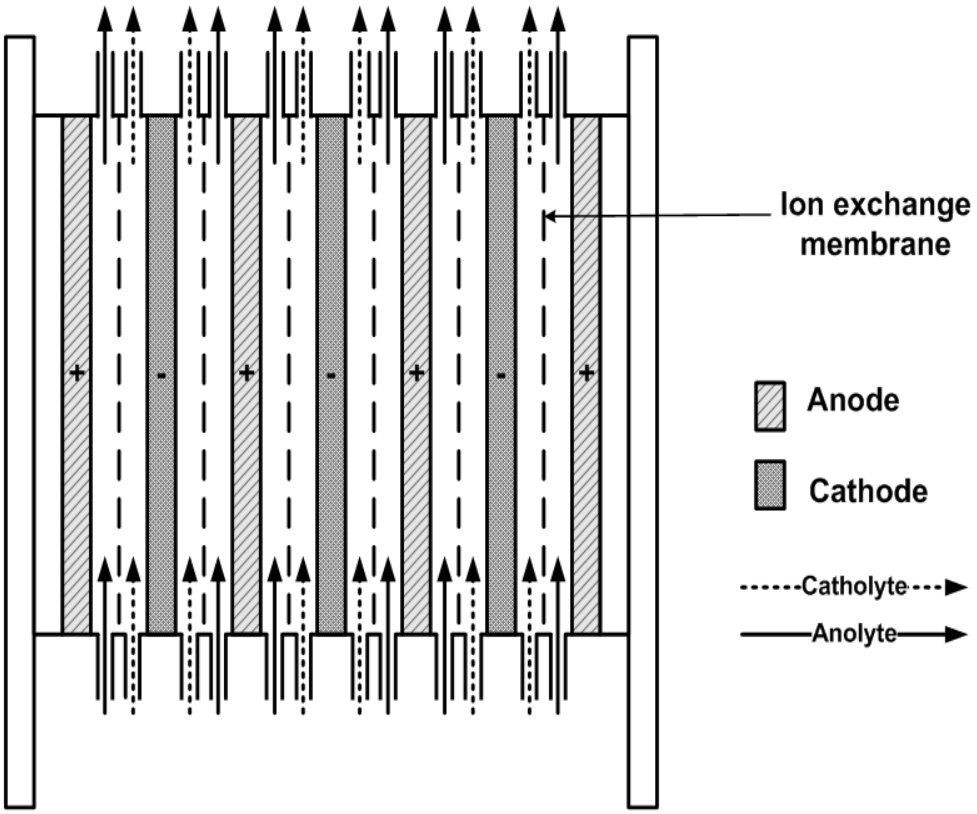

Figure 1.3 Parallel flow-by reactor with six electrode pairs (electrical circuits excluded).

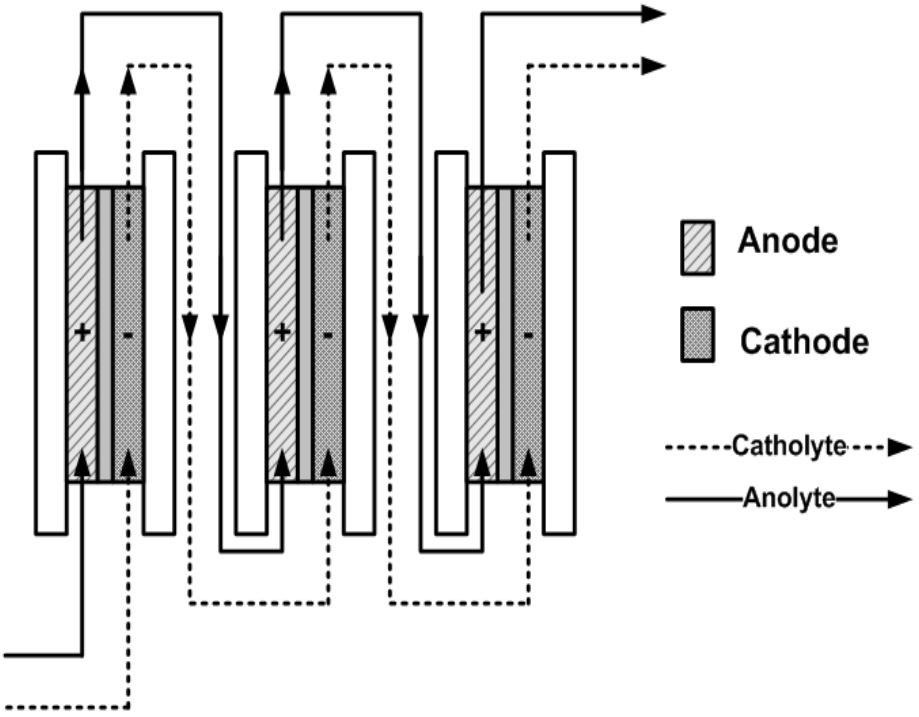

Figure 1.4. Flow-by reactor connected in series (electrical circuits excluded).

1.3.2 Three-dimensional Electrodes

The most important component in the electrochemical reactor is the electrode. The electrode can be broadly classified into two types, namely two or three-dimensional electrodes. These electrodes can be static or moving such as the rotating cylinder or rotating disc electrode. High mass transfer rates can be achieved with electrode movement while high surface area can be achieved with the use of porous, three-dimensional electrodes. Three-dimensional electrodes are more superior compared to two-dimensional electrodes when dealing with dilute process liquors due to the higher active electrode area per unit reactor volume leading to higher mass transfer rates even at low metal ion concentrations (Pletcher and Walsh, 1992; Walsh and Reade, 1994; Walsh, 2001). Examples of three-dimensional electrodes are porous graphite electrodes, carbon felts, reticulated vitreous carbon (RVC), packed bed electrodes and active fluidized bed electrodes. Studies involving these three-dimensional electrodes can be found extensively in the literature (Pletcher *et al.* 1991; Ponce-de- Leon and Pletcher, 1996; Widner *et al.* 1998).

1.3.2.1 Porous Graphite

Graphite is one of the allotropes carbon. It is composed of a series of stacked parallel layer planes shown schematically in Figure 1.5. Within each layer plane, each carbon atom is bonded to three others with sp^2 bonding, forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional molecule. The hybridized fourth valence electron is paired with another delocalized electron of the adjacent plane by a van der Waals bond. Graphite can conduct electricity due to the vast electron delocalization within the carbon layers. These valence electrons are free to move and hence able to conduct electricity.

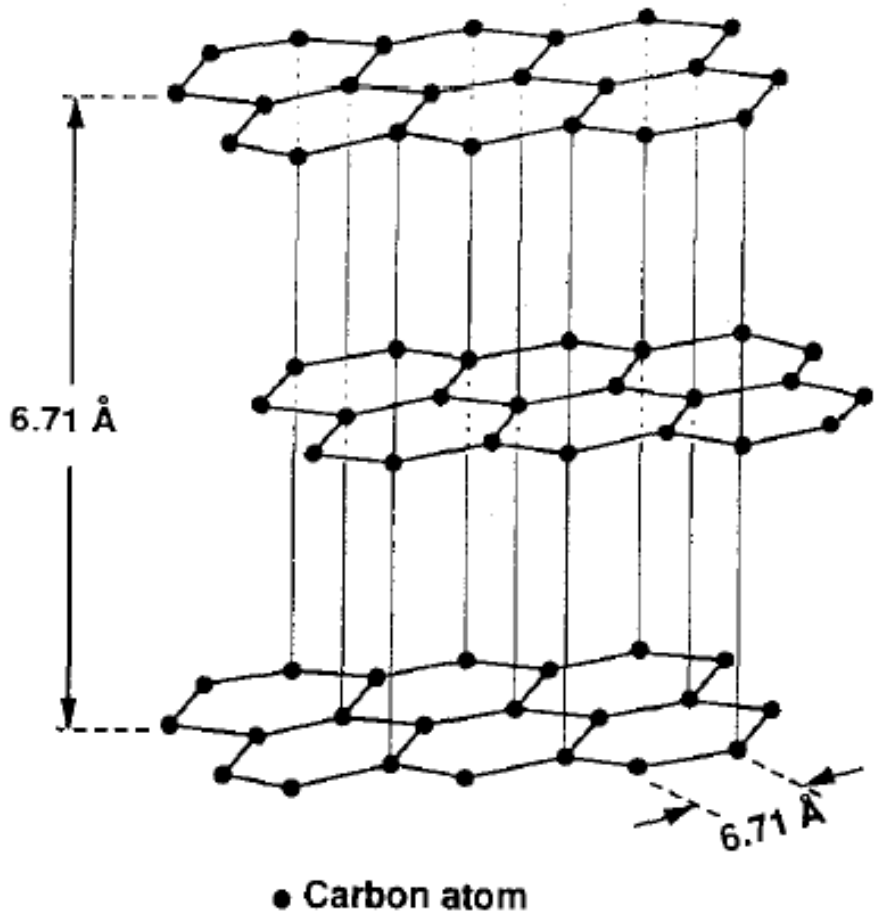

Figure 1.5 Three-dimensional schematic of the graphite structure (Pierson, 1993)

However, the electricity is only conducted within the plane of the layers. There are two known forms of graphite, *alpha* (hexagonal) and *beta* (rhombohedral) graphite which have very similar physical properties except that stacking of these layer planes occurs in two different ways (Pierson, 1993).

1.3.2.2 Reticulated Vitreous Carbon

RVC is an open pore foam material composed solely of vitreous carbon (Reticulated vitreous carbon- A new form of carbon, 2008). It has a honeycomb structure as shown by Figure 1.6. The structure of RVC is achieved by polymerisation of resin combined with foaming agents, followed by carbonisation. RVC is produced in several pore sizes, usually described as number of pores per inch (ppi). It has a free void volume between 90% and 97%, depending on the ppi grade and its three-dimensional porous structure offers high surface area, up to 66 cm^2/cm^3 for the 100 ppi RVC (Wang, 1981; Friedrich *et al.*, 2004**)**. It is suitable to use RVC as an electrode material especially in flow reactors which require high void volume, high surface area and low electrical and fluid flow resistance. RVC is one of the most chemically inert forms of carbon over a wide range of temperatures. Its chemical inertness, its wide range of usable potential (1.2 to -1.0 V *vs*. SCE) and the hydrodynamic and structural advantages of its open-pore foam structure make vitreous carbon foam an attractive material for electrodes (Wang, 1981). However, the skeletal structure of the material is brittle and needs support and the low volumetric carbon content means that care has to be taken to ensure uniform potential and current distribution through the material.

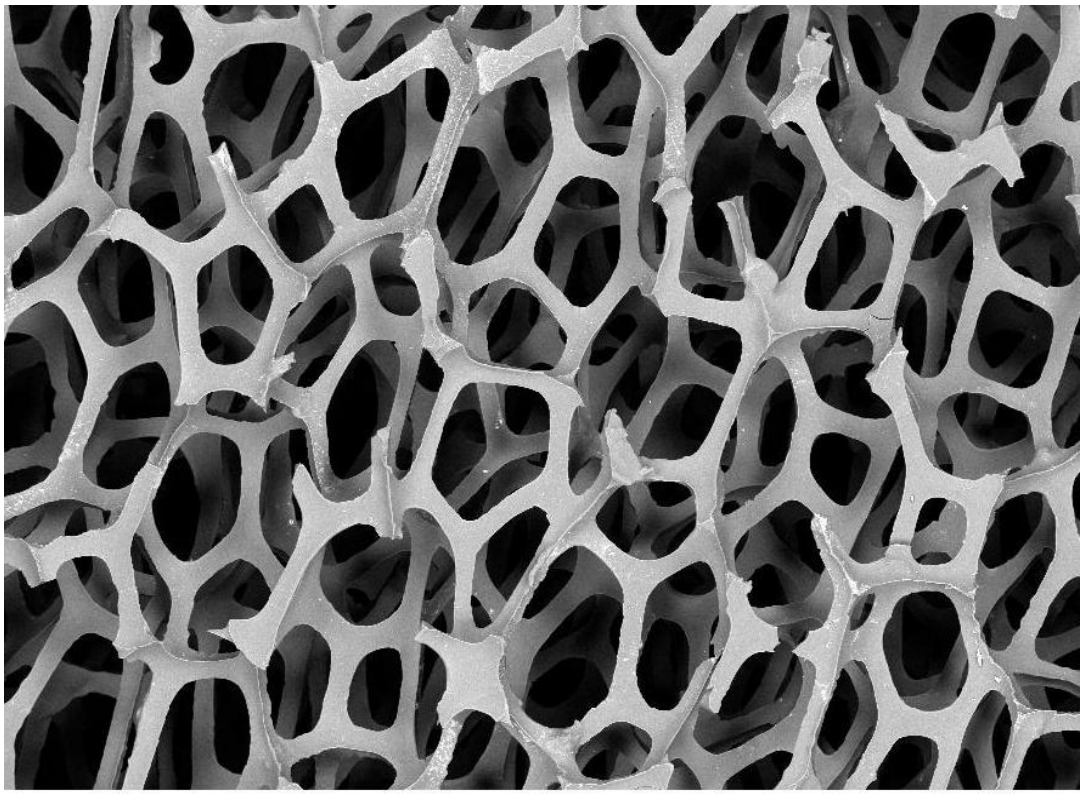

Figure 1.6 SEM micrograph that shows the three-dimensional honeycomb structure of RVC at 50x magnification

1.3.3 Electrochemical Reactor Design with Three-dimensional Electrodes

In electrochemical reactor design, achievement of efficient mass transport is necessary since the maximum current density for a reaction is directly proportional to mass transport coefficient. Efficient mass transport will minimize the differences in the composition of chemical species adjacent to electrode surface and bulk solution. The rate of reaction in a mass transport controlled process depends on the rate at which a particular species reaches the electrode surface. A high mass transport coefficient is favourable when dealing with dilute solutions. Apart from increasing the volumetric flow rate of the electrolyte passing through the reactor, mass transport can be increased by installation of turbulence promoters placed in the flow path of electrolyte. The turbulence promoters can increase local eddy currents and increase mass transport. Turbulence promoters also encourage uniform current and potential distributions by promoting mixing between the boundary layer and the bulk solution (Pletcher, 1992).

The charge transport within an electrolyte solution depends on ionic conduction. The ionic conduction is described by physicochemical laws and quantities, where conductivity, ionic dissociation, ion mobility and transport number are each playing their own roles. The charge transport process also influences the current distribution on the electrode in the reactor. A non-uniform current density will decrease the current efficiency in the process. The main factors which influence current distribution is conductivity of the electrolyte, geometry and dimension of the electrode, activation overpotential at the electrode which depends on electrode kinetics and concentration overpotential which depends on the mass transport process. Because the potential distribution within an electrode is strictly correlated

with current distribution and the selectivity of redox reactions depends strongly on the potential applied to the surface, it is essential to ensure uniformity of the current distribution to increase current efficiency (Heitz and Kreysa, 1986).

The use of three-dimensional electrodes increases the reactor design complexities due to its non-uniform current and potential distribution (Pletcher and Walsh, 1992; Walsh, 2001). The performance of an electrochemical cell using a three-dimensional electrode is critically dependent on the potential distribution within the electrode and penetration depth of the current. The potential in the liquid phase, Φ_s and solid phase, Φ_m tend to be non-uniform along the direction of current flow, due to the ohmic drop. In thin electrodes, the potential falls slowly, the driving force (Φ_m-Φ_s) for electrochemical reaction becomes smaller towards the current collector (Figure 1.7 (a)). If the electrode is thick, the driving force will become so small that the reaction rate is under mixed or charge control and the current is very low (Figure 1.7 (b)).

Figure 1.8 shows that the potential distribution arises due to differences in liquid phase potential, Φ_s and solid phase potential, Φ_m in flow-through and flow-by reactors. For a flow-through porous electrode, if the electrode thickness is higher than effective penetration depth, theoretically very little of the porous electrode is operating under mass transport limiting conditions. Therefore, the effective electrode thickness is limited by a voltage drop. In a flow-by configuration, an ohmic drop occurs across the electrode thickness, electrode length can be extended to achieve a higher conversion per solution pass. It is important to note that distribution of potential, current density and flow are all interrelated in a three-dimensional

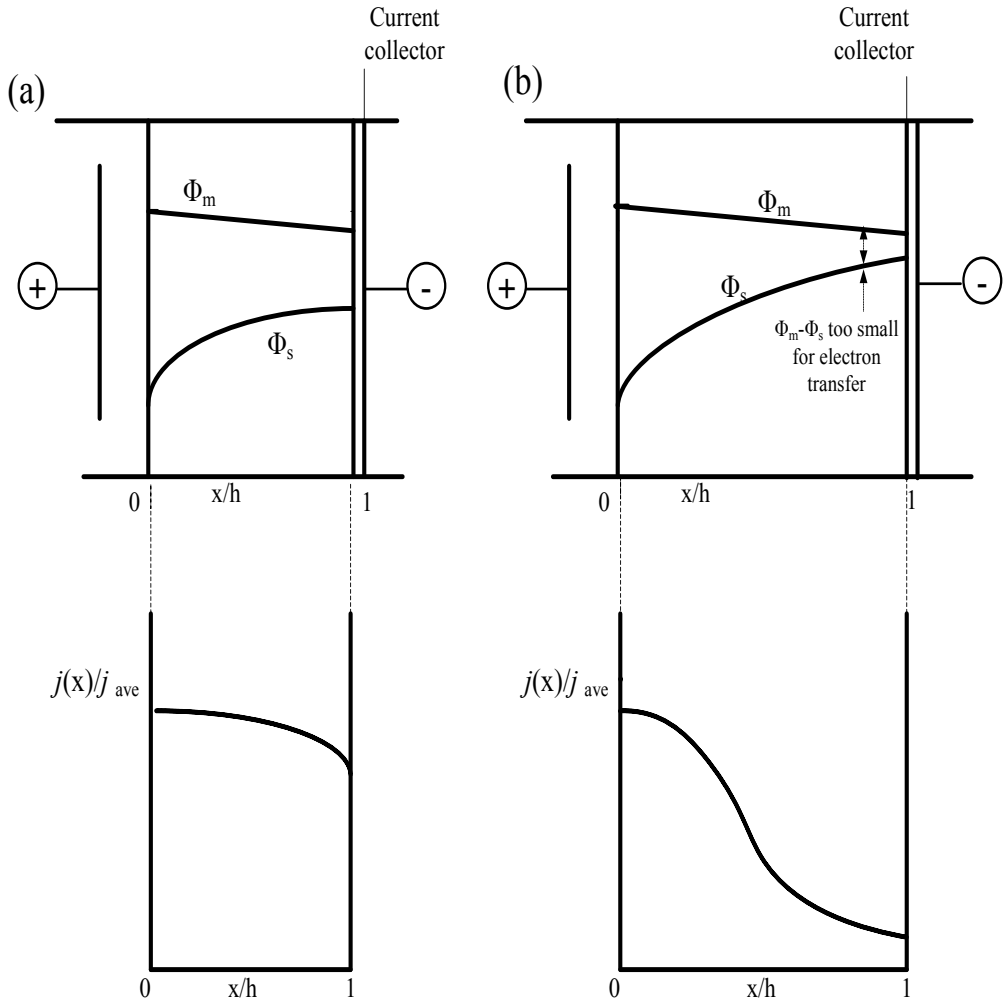

Figure 1.7 Electrode potential and normalized current density distribution in three-dimensional electrodes. (a) thin electrode (b) thick electrode. $j(x)$ is the local current density at point x and j_{ave} is the mean current density over all x (adapted from Pletcher and Walsh, 1992)

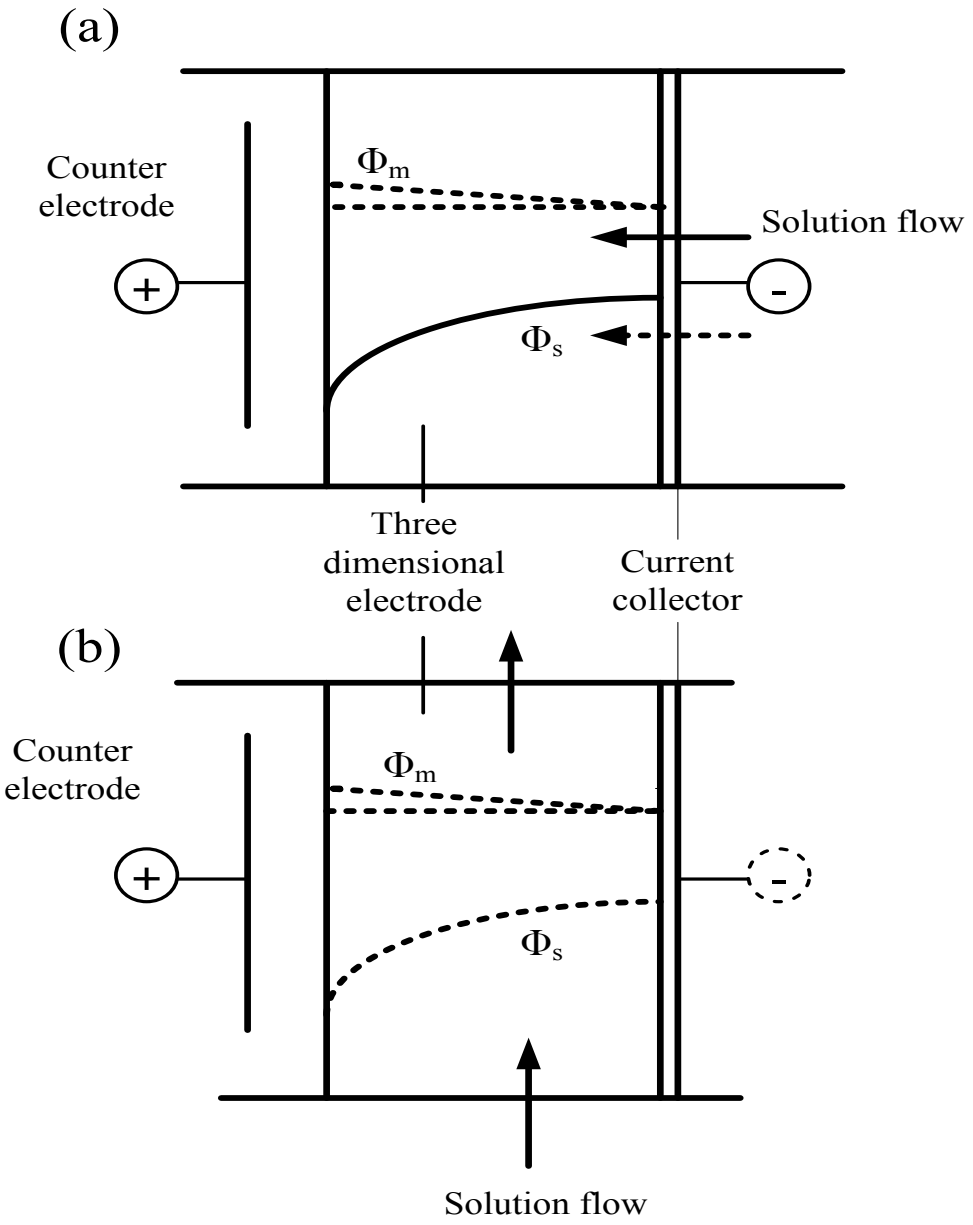

Figure. 1.8 Potential distribution in a three-dimensional electrode in (a) flow-through (b) flow-by reactor. Dotted line shows solid phase potential in case of an excellent current conductor, (Φ_m =constant)

electrode (Langlois and Coeuret, 1990; Pletcher and Walsh, 1992; Doherty *et al.*, 1996).

1.3.4 Ion Exchange Membrane

Another component which plays an important role in electrogenerative reactors is the ion exchange membrane. It works as a separator between the anolyte and catholyte of different compositions which enforces selectivity in the migration of ions between both compartments. The advantages of using ion permeable membranes as a separator are its high selectivity, high stability and high rate of transport of ions through the membrane thus achieving high conductivity with low resistance (Davis *et al.*, 1997). Other considerations involve the cost of the reactor, low maintenance requirements, simplicity of design and installation, safety and ease of operation. Placement of an ion exchange membrane in the reactor should be considered carefully to minimize the interelectrode gap, which leads to an ohmic loss. The cell design and operation mode are strongly dependent on the specific process application and objective of the operation.

1.3.5 Electrochemical Transport Process

Heterogeneous reduction of metal ions on the electrode will involve various transport processes. Mass transport, charge transfer processes must be taken into account in the studies of electrochemical reactors. Charge transfer determines the kinetics of the electrochemical reaction. Mass transport describes the transport of chemical species towards and away from the electrode surface; meanwhile charge transfer determines the current distribution in a reactor, influence the space time yield and the scale-up of electrochemical cell (Heitz and Kreysa, 1986).

1.3.5.1 Charge Transfer and Kinetics

The kinetics of an electrochemical process depends on the relationship between cell potential and current. The equilibrium potential is obtained by subtracting the potential of cathode to anode and is related to the free energy of the overall cell reaction as indicated by Eq 1.2.

However. Eq 1.2 does not taken into account the rate of reaction. The rate of reaction depends on the kinetics of the two electrode reactions. At equilibrium, the potential of an inert electrode in a solution containing both species O and R will be given by the following Nernst equation;

$$E = E^{o} + \frac{RT}{nF} \ln \frac{c_O}{c_R} \qquad (1.3)$$

When a potential other than the equilibrium potential is imposed on the electrode, current will pass and the ratio of c_O/c_R will change according to the Nernst equation. If the electrode is made positive with respect to E, anodic current will flow and if it is made negative with respect to E, a cathodic current which is due to the conversion of O to R will be observed. Since oxidation and reduction depend on the charge transfer across the electrode and electrolyte interface, the rate constant for the reaction will be influenced by the local potential field which drives the charge transport. When an electrochemical reaction is slow, an overpotential is needed to drive the reaction. There exists an exponential relationship between current density and overpotential. The measured current is described by Butler-Volmer the equation shown as below;

$$j = j_o \left(\frac{\exp((1-\alpha)nF\eta)}{RT} - \frac{\exp(-\alpha nF\eta)}{RT} \right) \quad (1.4)$$

Where j_o is exchange current density at the the equilibrium potential, α is charge transfer coefficient and η is overpotential. This equation shows that the kinetics of charge transfer depend on potential. Some electrode reactions are fast and give a reasonable current density close to the equilibrium potential. In contrast, others are slow and an overpotential is necessary to obtain a required current density. In most practical conditions, the potential will not be close to the equilibrium condition, one of the terms in this equation will be dominant. When the applied potential is negative with respect to equilibrium potential, the equation for the cathodic current becomes as follows;

$$-j_c = j_o \exp\left(\frac{-\alpha nF}{RT} \eta \right) \quad (1.5)$$

The equation can be written as:

$$\log j = \log j_o - \frac{\alpha nF}{2.3RT} \eta \quad (1.6)$$

which is also known as cathodic Tafel equation (Bard and Faulkner, 1980; Pletcher, 1992; Pletcher and Walsh, 1993).

1.3.5.2 Mass Transport

There are three forms of mass transport, namely diffusion, convection and migration (Pletcher, 1992). Diffusion is the movement of species down a concentration gradient and it is described by Fick‘s Law. An electrochemical reaction converts a reactant to a product at the surface of the electrode. There is a boundary layer adjacent to the electrode surface where the concentration of reactants and products in the boundary layer is lower and higher than the bulk solution respectively. Hence, reactants will diffuse from the bulk solution to the electrode surface and products will diffuse away from it.

Convection is the movement of species due to mechanical forces. It is normally induced by stirring of solutions, electrode rotation and electrolyte flowing through the reactor. Convection can be categorized as free and forced convection. If it is caused by external influence such as stirring, it is called forced convection; whereas if it occurs spontaneously due to temperature variations, it is called free convection.

Migration is the movement of charged spesies due to a potential gradient. The current of electrons through an external circuit must be balanced by the passage of ions through the membrane. If the reaction is carried out in a high concentration of inert electrolyte in solution, most of the charges will be carried by those inert species and less of the electroactive species is transported by migration.